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**OSMIUM ISOTOPIC RATIO MEASUREMENTS BY
INDUCTIVELY COUPLED PLASMA SOURCE MASS SPECTROMETRY**

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BRIEF

An osmium tetroxide generator coupled to an inductively coupled plasma source mass spectrometer was used to measure the isotopic composition of nanogram quantities of osmium. Precisions of <1% were obtained.

ABSTRACT

The isotopic composition of nanogram quantities of osmium were measured using an inductively coupled plasma source mass spectrometer. Sensitivity was enhanced a factor of ~100 by the use of an osmium tetroxide vapor generator rather than nebulization of solution. For samples ≤ 5 ng, the ratios $^{190}\text{Os}/^{192}\text{Os}$, $^{189}\text{Os}/^{192}\text{Os}$, and $^{188}\text{Os}/^{192}\text{Os}$ were determined to better than $\pm 0.5\%$ (1 σ) precision. For the minor isotopes, the ratios $^{187}\text{Os}/^{192}\text{Os}$ and $^{186}\text{Os}/^{192}\text{Os}$ were determined to $\pm 1\%$, and $^{184}\text{Os}/^{192}\text{Os}$ (4×10^{-4}) was determined to $\sim 10\%$. Isotope ratios for common osmium are reported.

INTRODUCTION

The ability to measure the isotopic composition of nanogram or smaller quantities of osmium is necessary for the development of the ^{187}Re - ^{187}Os dating technique for geological samples and would provide a sensitive method of measuring osmium concentrations in rocks or other materials by isotope dilution. Such measurements have been hampered by the difficulties in isolating osmium from samples and finding suitable mass spectrometric techniques. It has been shown that osmium isotopic measurements can be made with an ion microprobe (1,2). However osmium isotopic assay by ion microprobes requires extensive sample preparation. The collected spectra are subject to polyatomic ion interferences, and the equipment is expensive and not widely available. Measurements have also been made with the Laser Microprobe Mass Analyzer (LAMMA) (3), but in addition to having the same problems as the ion probe, interpretation of LAMMA spectra was complicated by severe non-linearities in the detector system. Recently there have been reports of osmium isotopic ratio measurements by resonance ionization mass spectrometry (4) and accelerator mass spectrometry (5). As part of a project to measure the ^{187}Re half life (4.35×10^{10} y) (6), we investigated inductively coupled plasma source mass spectrometry (ICP-MS) (7) as a tool for making such measurements.

In ICP-MS, samples are usually liquids which are introduced into the plasma by means of a nebulizer and spray chamber. Even though this process is only ~1% efficient, the detection

limits for many elements including the noble metals are at the <0.1 ppb level using commercially available instruments (8,9). In spite of this high sensitivity, it was obvious that for nanogram sized samples it would be necessary to avoid the inefficiency of nebulization. Bazan (10) has shown that an enhanced osmium signal could be obtained in inductively coupled plasma optical emission spectroscopy (ICP-OES) by use of an osmium tetroxide generator which was used to produce the volatile OsO_4 and introduce it, essentially free of solvent, directly into the plasma. We report here the technique of coupling the osmium tetroxide generator to an ICP-MS, and the details of analyses of common osmium performed in connection with the measurement of the half life of ^{187}Re (6).

EXPERIMENTAL SECTION

All measurements were made on the prototype ICP-MS at the British Geological Survey. This instrument, which has been described elsewhere (7), is a precursor of the Plasmaquad manufactured by VG Isotopes. OsO_4 was generated in the samples and sparged from solution with the "discrete batch" sampling system described by Bazan (10). The overall configuration of the system is shown in Figure 1. To prevent loss of osmium from solution prior to analysis, samples were stored either dry or in ≥ 3 N HCl solution. Before analysis, dried samples were redissolved in HCl then made basic with ammonia solution. Previous work using ICP-OES had shown that more signal was obtained if before samples were analyzed, they were allowed to sit overnight after being made ammoniacal. This practice was

continued for the ICP-MS work. Analyses were also made by solution nebulization to compare the efficiencies of the two techniques and to evaluate their susceptibility to interferences. The uptake rate of the nebulizer was ~2.2 mL/min., and ~1% of the sample was delivered to the torch.

With the batch sparging system, the torch could be isolated from the sample-carrier gas line. This allowed the plasma to be maintained and hence the mass spectrometer to be left in the operating mode while samples were being changed. Between samples the generator including the condenser was washed with water injected through the stopcock at the top of the apparatus and drained from the bottom. The generator was then flushed with Ar which was allowed to escape out the top. Next the oxidizing agent (10 wt. % HIO_4 in H_2O) was introduced into the chamber with a teflon tube inserted through the sample injection port. This was followed by the injection of the sample solution through the same port. To avoid problems with plasma instability when the generator was opened to the torch, care was taken to avoid the introduction of excessive quantities of air into the sparging chamber. After closing the sample injection port, the stopcock isolating the generator from the torch was opened. The sparging Ar valve was opened. The heating coil was switched on, and data collection was begun. Typically 1 mL each of oxidizing agent and sample were used.

The mass spectrometer was operated in a single region, scanning mode which scanned the selected mass region once per second. Scans typically covered the range of 184-194 amu and

were stored in 1024 channels of a multichannel analyzer operated in the multiscaling mode. Successive sweeps were summed for periods of five minutes. Typically four accumulations (20 min total) were made per sample. Having the sample released over a period of minutes and collecting several spectra per sample offered several advantages. (1) It was possible to examine the data for variations in isotopic composition as a function of time. (2) One could decide after the fact whether to discard end of run data on the basis of the signal to background ratio. (3) The instrument could be adjusted if necessary, and (4) if there was a problem with data storage, all the information on a sample was not lost. Isotope ratios were calculated from the total number of counts collected under each peak.

It was found that after a period of minutes, white crystals sometimes formed on and clogged the frit at the bottom of the reaction flask. This prevented the flow of the sparging gas. In subsequent work, this problem was overcome without loss of sensitivity by reducing the $[HIO_4]$ to 2.5 %. The plasma torch was operated under the following conditions: power 1.25 KW, coolant gas flow 13 L/min, auxiliary gas flow 0.4 L/min, sample-carrier gas flow 0.85 L/min, and sparging gas flow 0.2 L/min. The pressure on the sample-carrier and sparging gas lines was 20 psi before the flow meters. The sensitivity of the system was strongly dependent on the sum of the gases carrying the sample to the torch. Their flow was set to maximize the observed ion beam. The relatively high auxiliary flow was necessary to prevent the tip of the torch from overheating due to the dry

sample gas. The diameter of the hole in the aperture used to admit ions to the mass spectrometer was 0.6 mm. Reagents were analytical grade and H₂O was distilled or deionized. Two supplies of natural osmium were analyzed.

RESULTS AND DISCUSSION

A comparison of the sensitivity of nebulization and sparging for osmium analyses is shown in Figure 2. An accurate comparison of sensitivities by the two methods was not attempted, but the sparging method is ~100 times more sensitive. This is the factor expected on the basis of the nebulizer's efficiency. On the other hand, part of the improvement may be related to the use of a dry plasma; i.e., solvent cooling of the plasma has been minimized (11). The sparging spectrum of Figure 2 is the summation of four five-minute data accumulations for a 10 ng sample. Individual accumulations for a 1 ng sample are shown in Figure 3. One sees that the signal reached its maximum intensity after a period of about five minutes and then gradually decreased. For this sample, data collection was stopped after 20 min because the additional precision which could have been achieved by continued data accumulation would have been insignificant. An expanded view of the baseline obtained using the sparging system and 5 ng of osmium is shown in Figure 4 for the mass region 170-218 amu. Several important qualitative observations can be made from the raw spectra. (I) One ng of Os is readily detectable and gives a signal which lasts for ≥20 min before the background becomes dominant at the 186 and 187 peaks

which are each present at the 16 pg level. As pointed out above, a long duration signal was desirable to test for temporal variations in the isotopic ratios and to minimize the risk of data loss inherent in transient signals. Extending the signal over such a long time increases the background correction due to random pulses in the system, but the background was low enough (~14 cpm under each peak) not to be a major concern for the time intervals involved. (II) The peaks are baseline resolved so overlaps need not be considered. (III) No peaks are observed at masses 183, 185, 191, or 193. The absence of a peak at 183 shows that no corrections were necessary for W ions, which could isobarically interfere with Os at masses 184 and 186. Although not shown in the figures, W ions were observed in some analyses of Os by nebulization and seriously interfered at mass 186. The lack of a peak at mass 185 shows both that Re ions were not detected and therefore can not be interfering at mass 187, and that no polyatomic ion peak was present at mass 185 which would compromise the ability to use 185 as a monitor for Re contamination. In that a common method used to separate Os from Re is to distill the Os (12), one would not expect Re to be carried into the torch with Os. However, because the abundance of ^{187}Os is the critical quantity to be measured for ^{187}Re - ^{187}Os chronology studies, it is important to monitor for Re interference in Os spectra. The absence of peaks at masses 191 and 193 show that Ir is not present and that these peaks can be used as measures of the background signal to be subtracted from the other peaks. (IV) In Figure 4 the ^{184}Os

peak is clearly observable above the background even though it is present in the sample at only the 1 pg level. (V) There are minor peaks present at the masses of the Pt, Hg, and Pb isotopes, and these peaks occur in ratios consistent with the presence of small ion beams of those elements. The presence of Pt will cause interferences at masses 190 and 192. For the work reported here these interferences are negligible ($\leq 0.1\%$), but for the analysis of $\ll 1$ ng of Os they could be important. The origin of these contaminants is unclear. They have been observed in three different ICP-MS systems and in spectra from different Os sources prepared with different reagents. It is possible these elements are present in the HIO_4 which was from a common source. How these elements reach the mass spectrometer has not yet been investigated, but their presence in the Os spectra may indicate interesting analytical applications.

Peak areas for each accumulation were calculated by summing the observed counts in the MCA channels corresponding to the peaks. The same number of channels was used for each peak. The average of the counts at 185, 193, and the mass corresponding to the beginning of the scan region (~ 183) was subtracted from each of the other masses to correct for instrumental background. Reagent blanks were analyzed between measurements of the osmium samples to establish that memory was not contributing to the background of the samples.

Isotope ratios were calculated from the background corrected count rates. No correction was made for dead time in the counting system because of the low count rates involved ($< 10^4$

cps). It was found that the isotope ratios measured for the individual accumulations from a single sample did not vary. The individual accumulations were therefore summed and the uncertainty on the measurements calculated as the square root of the number of ions observed.

As shown in Figure 5, the observed isotope ratios, calculated relative to the signal at mass 192, deviated from the values of Nier (13) linearly as a function of the mass difference between the isotopes. This deviation is ~ 1.5 %/amu, favors loss of the lighter isotopes, and varies slightly from sample to sample. The details of the deviation's origin are unclear, but probably relates to the transmission of the quadrupole mass spectrometer. To correct for this effect and be consistent with Nier (13) and Luck and Allégre (2), the measured isotope ratios, $(M/192)_m$, were normalized to a constant value of $(188/192)_t = 0.3244$ by the formula

$$(M/192)_m = (M/192)_t \{1 + B \cdot (192 - A)\} \quad (1)$$

where $(M/192)_t$ is the true (i.e., corrected ratio), B is the bias per mass unit determined from the $(188/192)_m$ for the sample, and A is the mass of the isotope being "ratioed" to 192. The observed value of B for 12 analyses of 1-5 ng each are shown in Figure 6. As judged by the counting statistics uncertainties of the ratios, these data, which were collected over a period of four days, show sample to sample variations in the extent of mass bias and show the desirability of being able to make the correction on the basis of a known pair of isotopes within

the sample. However, the variation is small enough to apply the average mass bias to all samples without seriously degrading the results for the other isotopes. Furthermore, the variation from sample to sample within a period of hours and under the same running conditions is smaller than the overall variation. This would allow one to analyze a standard followed by an unknown and apply the mass bias factor of the standard to the unknown. This feature was important for the measurement of the half life of ^{187}Re (6) because those samples had no isotope pair in a well known ratio.

Figure 7 summarizes the mass bias corrected data for the ratios $^{180}\text{Os}/^{182}\text{Os}$, $^{183}\text{Os}/^{182}\text{Os}$, $^{186}\text{Os}/^{182}\text{Os}$, and $^{184}\text{Os}/^{182}\text{Os}$ in the same 12 samples. At these low count rates, counting statistics uncertainties adequately describe the precision of the analyses. The data appear normally distributed. For a 5 ng sample, the typical uncertainty on the $^{180}\text{Os}/^{182}\text{Os}$ and $^{183}\text{Os}/^{182}\text{Os}$ ratios is $\leq \pm 0.5\%$. The uncertainty on the $^{186}\text{Os}/^{182}\text{Os}$ ratios is approximately $\pm 1\%$, and $^{184}\text{Os}/^{182}\text{Os}$ is determined to $\sim \pm 10\%$. For 1 ng samples the uncertainties are roughly twice as large. These ratios, which are expected not to vary in nature, agree with the values of Nier (13) within the uncertainties. The agreement with Luck and Allégre (2) is not as good particularly at masses 186 and 184.

The number of ions collected per ng of sample varied in these samples within the range $(9-26) \times 10^4$. Part of this variation may be due to a loss of osmium from the dried samples,

and part may be due to variations in instrumental sensitivity. Whatever the reason, such variations limit the usefulness of the technique for concentration measurements except when isotope dilution is used. For isotope ratio work, the precision of the measurements depends somewhat on beam intensity, but accuracy does not.

The abundance of ^{187}Os relative to the other isotopes in a sample depends on the age and Re/Os ratio of the source rock from which the Os was extracted. Figure 8 compares the $^{187}\text{Os}/^{182}\text{Os}$ ratios obtained from two sources. Sample A is the one from which the data in Fig. 6 and 7 were obtained and the upper 12 values in Figure 8 are for the same analyses. Sample B and the last two determinations of A were measured at an earlier time when the sensitivity of the mass spectrometer was lower. In spite of the poorer precision of the earlier data and some scatter in the data, one can clearly see that sample B is $\sim 50\%$ enriched in ^{187}Os relative sample A. For a 1 ng sample, this enrichment is a $\sim 7\sigma$ effect at the poorer precision or a $\sim 20\sigma$ effect at the better precision.

In the process of determining the ^{187}Re half life (6), it was necessary to measure the isotopic composition of <1 ng of osmium per sample. These samples were essentially free of normal osmium. They contained only ^{187}Os resulting from ^{187}Re decay and selected osmium isotopes added to the Re reservoir, relative to which the ingrown ^{187}Os could be measured. When the samples were analyzed, the ratios were observed to vary from one data accumulation to the next due to the emergence during the

analysis of a natural osmium contamination. This contamination, which was low in the first few minutes of an analysis, increased for ~15 min and remained essentially constant for tens of minutes after that. In the worst case, the contaminant signal at mass 192 reached ~1000 cpm. From the isotopic composition of the contamination, it was possible to determine that this problem resulted from previous work done with the same torch at much higher osmium concentrations ($\mu\text{g's mL}^{-1}$) rather than accumulation of material from the immediately preceding analyses. Residual Os on the torch had been remobilized by oxidizing species carried over from the generator. The problem was most severe in a sample in HCl which had not been made ammoniacal.

For the half life work, it was possible to determine the desired ratios correctly by treating the problem as a two component mixture in which one component, the sample, was essentially free of ^{188}Os and the other component was natural osmium. When $^{187}\text{Os}/^{190}\text{Os}$ was plotted against $^{188}\text{Os}/^{190}\text{Os}$ for each accumulation, the data defined a well constrained mixing line from which the known (near zero) value of $^{188}\text{Os}/^{190}\text{Os}$ in the sample was used to determine the correct $^{187}\text{Os}/^{190}\text{Os}$ for the sample.

In natural samples, where ^{187}Os is the only isotope varying in relative concentration from sample to sample, this technique could not be used. However, if proper care is exercised, it is unlikely that such memory effects would be significant, and their presence can be determined by testing the

ratio of ^{187}Os to some other osmium isotope for variations during the analysis. In that the contaminant osmium is evolved slower than the sample, it is also important that measurements of blanks made between analyses be continued long enough to detect the contamination; i.e., at least 20 minutes. Making the original solution ammoniacal may not prevent contamination from accumulating on the torch, but it seems to suppress remobilization.

CONCLUSIONS

The ability to measure osmium isotopic ratios to precisions and accuracies of a few tenths of a percent has been demonstrated for quantities of ≤ 5 ng of the element. All osmium isotopes were measured. Spectra were free of polyatomic ion interferences, and peaks were baseline resolved.

The data presented here have been ratioed to the abundance of ^{192}Os because it is the most abundant isotope. Because ^{192}Os is also the most massive isotope, in ^{187}Os determinations the bias correction contributes more to the uncertainty in that measurement than necessary. For chronology applications, it would be preferable to ratio the isotopes to ^{188}Os and to use the $^{192}\text{Os}/^{188}\text{Os}$ ratio for the bias correction. This choice offers the advantages that both ^{188}Os and ^{192}Os are high abundance isotopes so the mass bias can be measured precisely and the mass separation between ^{187}Os and the reference isotope is minimized further reducing the magnitude of the correction. For a system such as ICP-MS with

good dynamic range in the detector and interference free spectra, the use of ^{188}Os as the reference isotope is less desirable because of its lower abundance, which inherently leads to lower precision measurements. Isotope dilution concentration measurements could be made by adding known quantities of any of the other stable isotopes.

No attempt was made to measure samples smaller than 1 ng, but based on the data for ^{184}Os , it should be possible with no changes in procedure to measure the $^{187}\text{Os}/^{188}\text{Os}$ ratio to a precision of $\pm 10\%$ in a sample of 50 pg of common osmium. The combination of sensitivity and precision make ICP-MS a strong candidate for use in ^{187}Re - ^{187}Os chronology studies. Fortunately those samples which have the lowest osmium concentrations are often also the ones expected to have the highest fraction of radiogenic ^{187}Os (14). In cases with large enrichments, less experimental precision is required in the ratio measurements.

Based on the number of ions observed per ng and the width of the mass scan, the number of osmium ions detected was 1×10^{-6} of the atoms in the sample. Several improvements in sensitivity and precision can be anticipated. The ICP-MS in our laboratory at Livermore is currently >5 times more sensitive in the nebulization mode than the instrument used in this work was when this work was done. Although not yet demonstrated, this improvement is expected to apply to osmium analyses with the tetroxide generator. In addition peak jumping software is being developed which will allow one to spend different amounts of

time on different isotopes and to skip over masses for which data are not required rather than scan at a constant speed through a continuous mass region. This should increase the precision of the $^{187}/^{188}$ measurements by about a factor of two.

The average ratios for the twelve analyses (≤ 5 ng each) of normal or common osmium plotted individually in Figure 7 are shown in Table I. Within the constraint of being normalized to a constant value of $^{188}\text{Os}/^{192}\text{Os} = 0.3244$, these values are our best estimate of the relative abundances of the osmium isotopes in natural samples. Although ^{187}Os has been included in the table, its abundance is expected to vary from sample to sample due to ^{187}Re decay, and the value reported here has no significance beyond this particular sample. For comparison the values of Nier (13) and Luck and Allègre (2) have been included in the table. Assuming uncertainties in Nier's values of ± 1 in the least significant digit reported, our ratios for all isotopes agree with his within 1.5σ . The agreement with Luck and Allègre is not as good. The most significant difference is at mass 186 where their value is higher than ours by five times the standard deviation of our ratio. In the three cases (^{188}Os , ^{189}Os , and ^{184}Os) where the disagreement exceeds 2σ of our values, the Luck and Allègre value is the higher. The precisions quoted by Luck and Allègre are better than those for the work presented here, but one should remember that our intention was only to show ng capability. Higher precisions, particularly for the minor isotopes, should be obtainable by analyzing larger samples. This should be done to better constrain the isotopic composition of normal osmium.

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TABLE I

Isotopic Composition of Natural Osmium

	190/192	189/192	188/192	187/192 ^a	186/192	184/192
Meas. 1 σ _m	0.6443 ^b ± 7	0.3955 ± 5	≡0.3244	0.03790 ^b ± 15	0.03842 ± 14	0.000474 ± 20
Nier ^c	0.644	0.394	0.324	0.0401	0.0387	0.00043
L+Ad ^d	0.6438 ± 3	0.39679 ± 13	≡0.3244	0.03687 ± 2	0.03907 ± 2	0.00058 ± 6

(a) Natural variation expected.

(b) One analysis rejected (dev. > 2 σ).

(c) Reference (13).

(d) Reference (2).

FIGURE CAPTIONS

Figure 1.

Schematic layout of the ICP-MS with the OsO₄ vapor generator attached.

Figure 2.

Mass spectra of the osmium region obtained for 10 ng of osmium by (a) nebulization of solution and (b) OsO₄ vapor generation.

Figure 3.

Four sequential 5 min data accumulations for a single ng of osmium.

Figure 4.

Mass spectrum obtained for 5 ng of osmium expanded to show the baseline and minor peaks. The width of the scan was wider than normally used to include neighboring mass regions.

Figure 5.

Deviation of measured isotope ratios from the values of Nier (13) as a function of the difference in mass between the isotope plotted and the reference isotope; i.e., 192. Data are for a single 5 ng sample. The slope of the correlation line would be different for other samples.

Figure 6.

Mass bias per amu calculated from the measured $^{188}\text{Os}/^{192}\text{Os}$. Samples are plotted as triangles if 1 ng and circles if 5 ng.

Figure 7.

Mass bias corrected ratios for isotopes not expected to vary in nature. Dashed lines are the values of Nier (13). Arrows indicate the values of Luck and Allégre (2). Points are plotted as in Figure 6.

Figure 8.

Mass bias corrected $^{187}\text{Os}/^{192}\text{Os}$ for a series of analyses of two different sources of natural osmium. 10 ng samples are plotted as squares. Others are as in Figure 6.

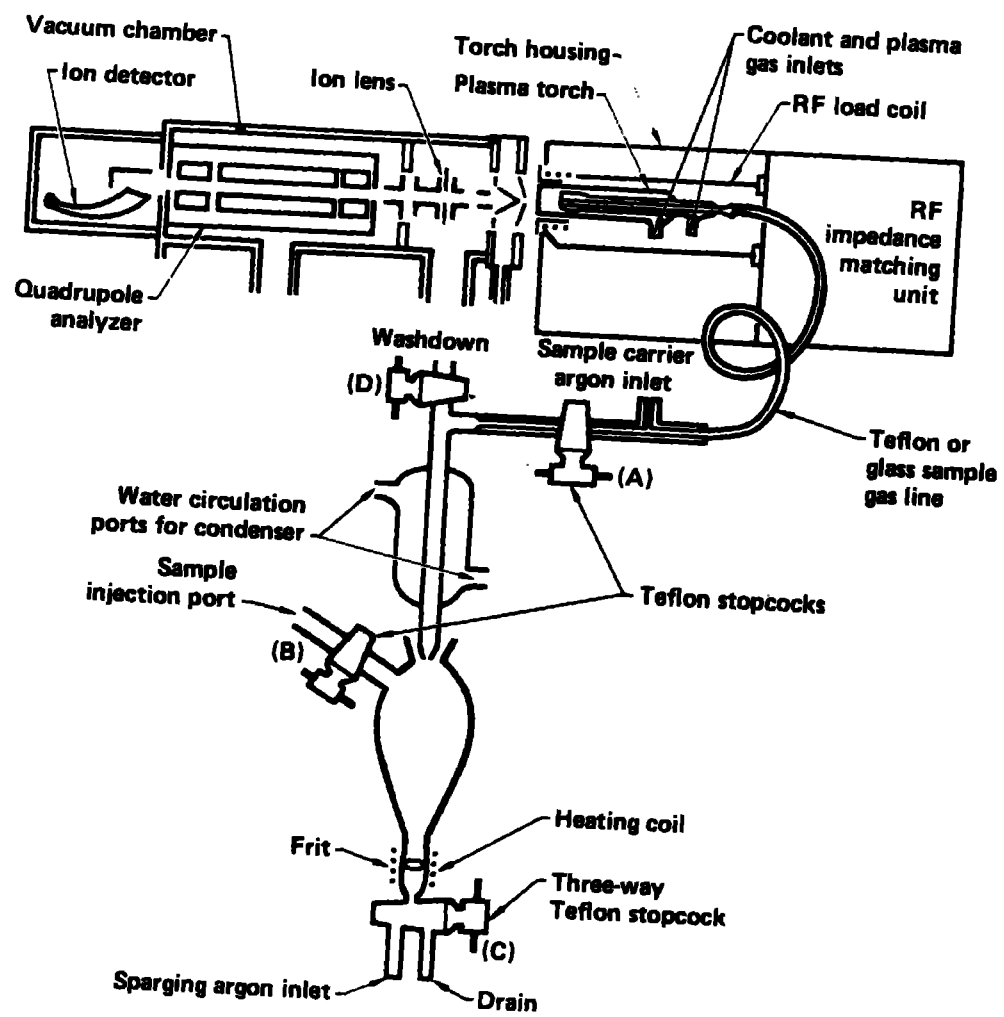


Figure 1.

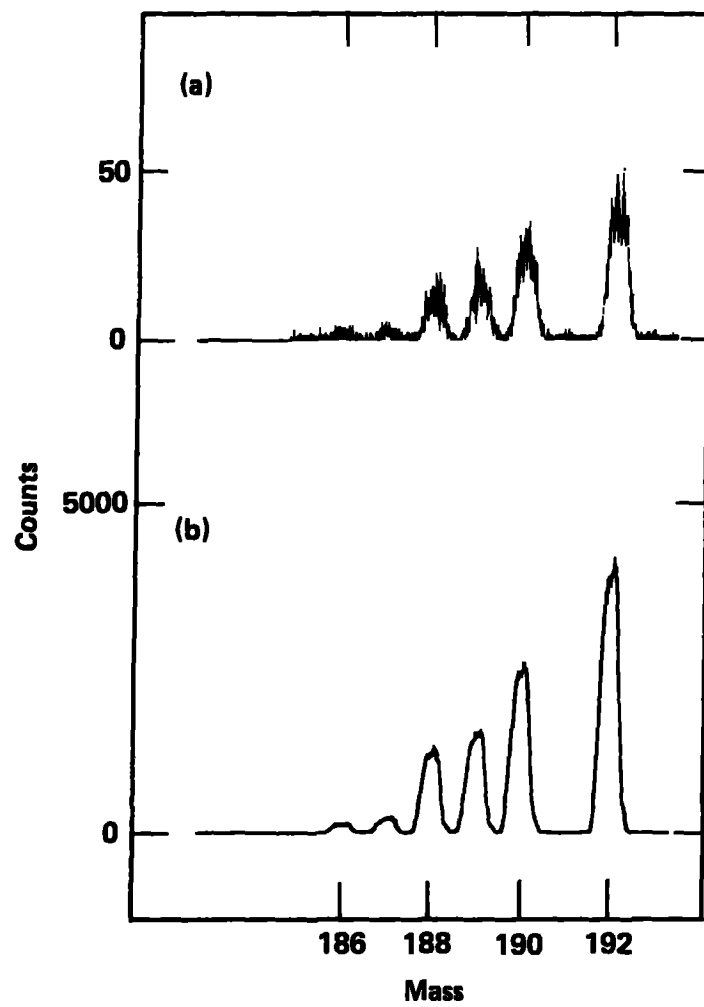


Figure 2.

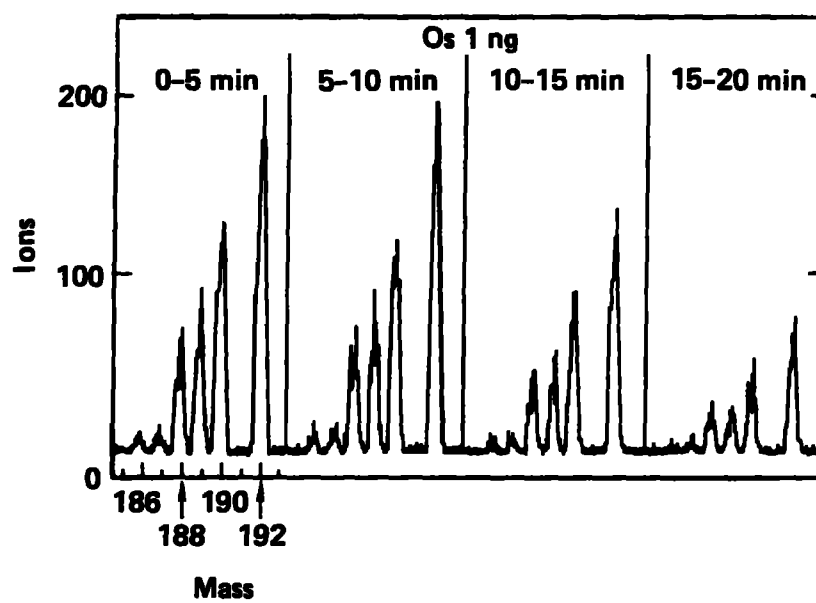


Figure 3.

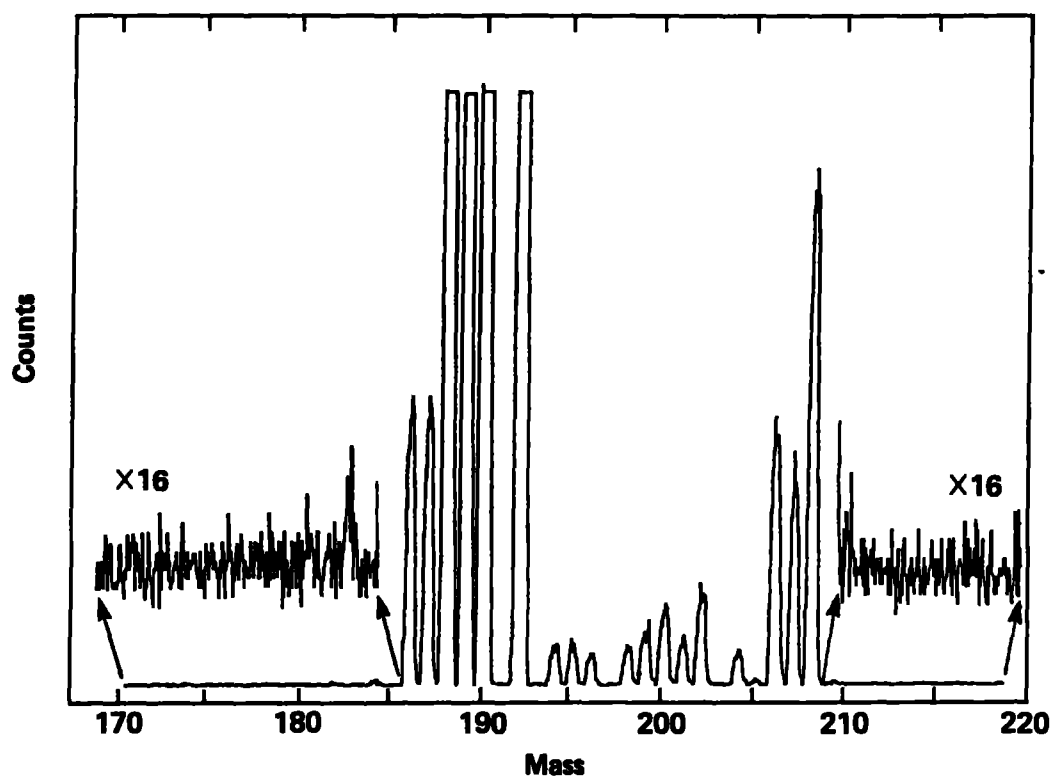


Figure 4.

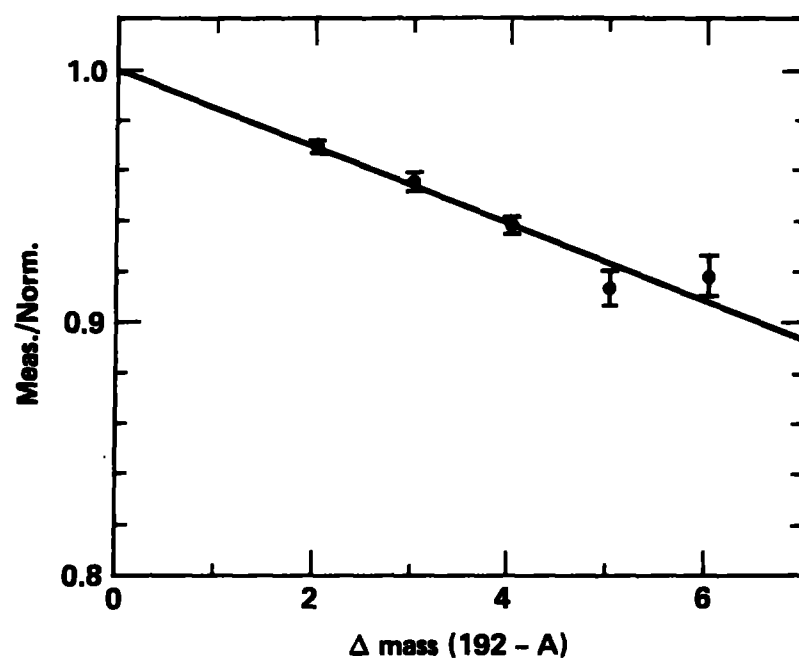


Figure 5.

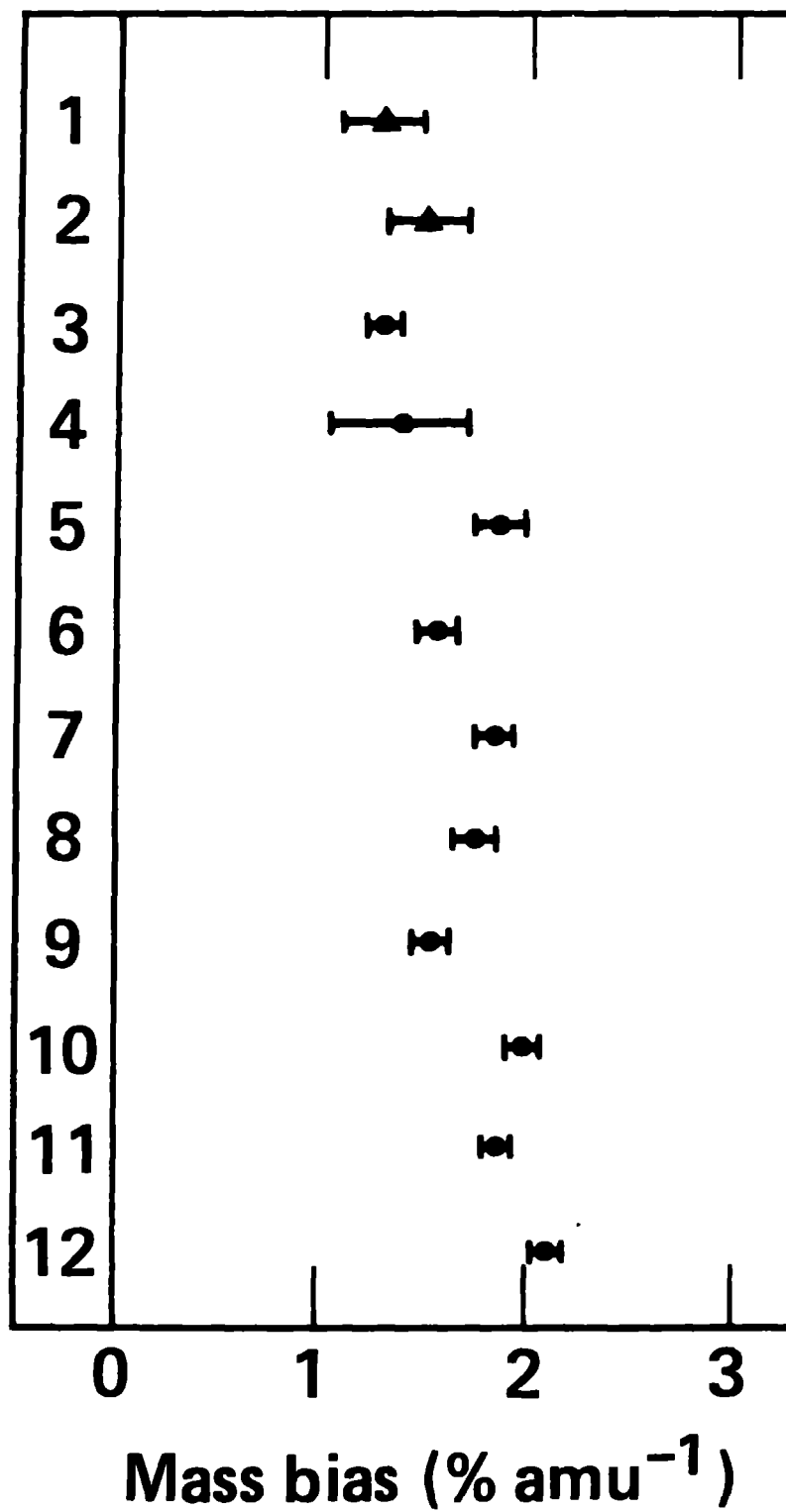


Figure 6.

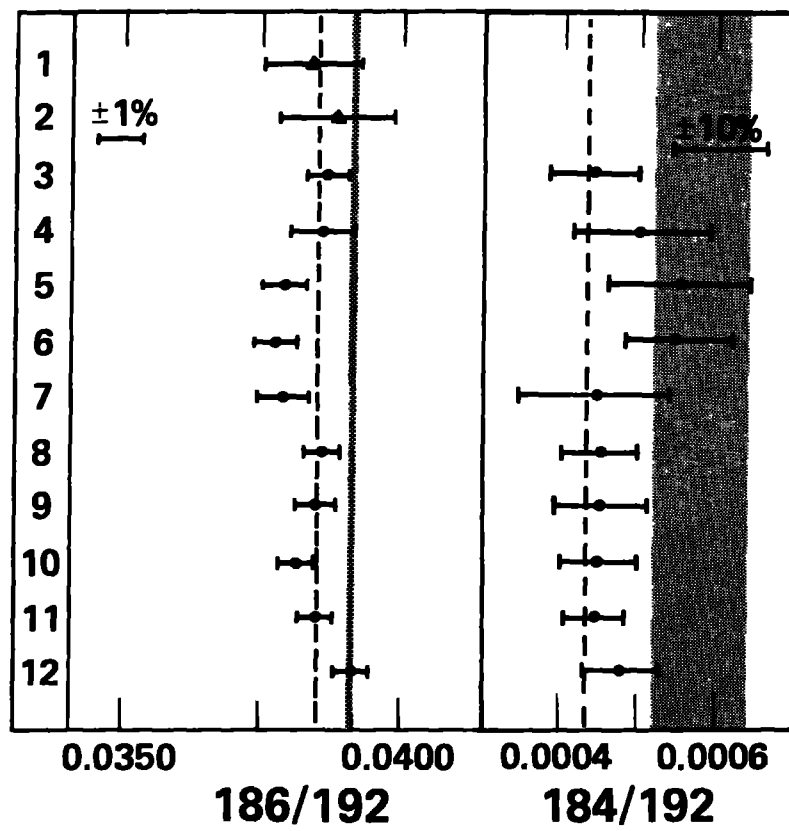
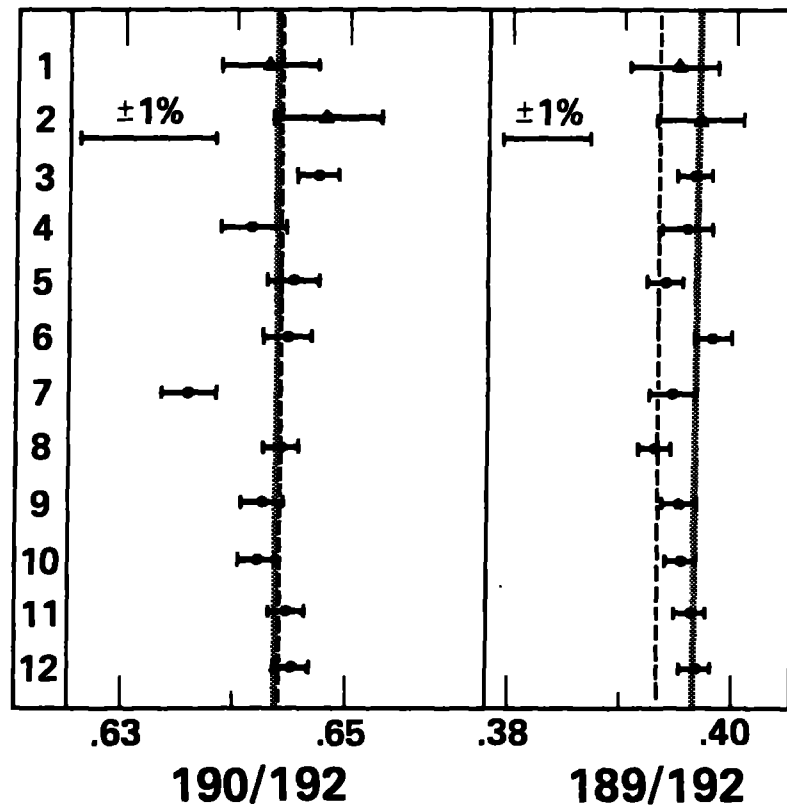


Figure 7.

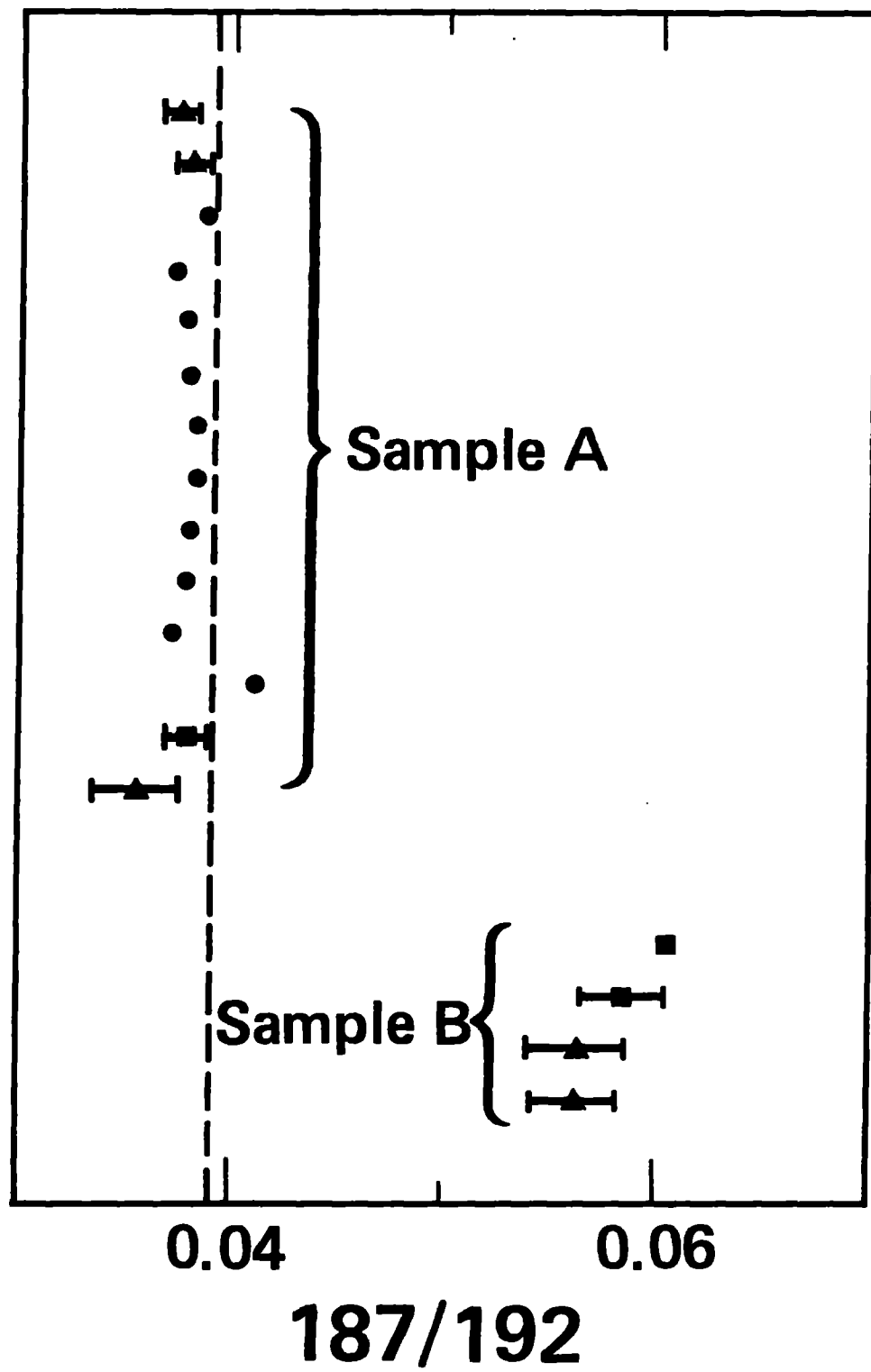


Figure 8.